Abstracts of the physico-chemical literature in Japan

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ABSTRACTS OF THE PHYSICO-CHEMICAL LITERATURE IN JAPAN

Vol. XVII　　November, 1943　　No. 6

1—GENERAL
(STRUCTURE—PROPERTIES—REACTIONS)

The molecular structure of fluore-, nonperoxyd. K. Higasi *Bull. Inst. Phys. Chem. Research*, **21**, 1147–1149 (1942).—The dipole efficiency is measured by the soln. method and found to be 3.1 D at 31°. From this result it is assumed that the molecule of that substance can be expressed not by a single constitutional formula but by a quantum mech. resonance among several substances.

J. C. L.

0°C- and 100°C-isotherms of helium, hydrogen, neon, argon, air, and carbon dioxide at pressures below two atmospheres, and the absolute temperature of 0°C. J. Ōisi. *Bull. Inst. Phys. Chem. Research*, **22**, 1119–1133 (1942).—0° and 100°-isotherms at pressures below two atmospheres were determined. These equations may be written as follows: $(pv)_0=a_0+\varkappa_0 p$, $(pv)_{100}=a_{100}+\varkappa_{100}p$. Then T_0, the absolute temp. of 0°C, is given by the equation: $T_0=100\,\frac{a_0}{a_{100}-a_0}$. The values of T_0 obtained are grouped in the following table.

Gas	T_0
He	273.15
H_2	273.15
Ne	273.14
A	273.16
Air	273.14
CO_2	273.15
mean	273.15

Considering the data obtained since 1929, the best value of T_0 is taken as $T_0=273.155\pm 0.015°$.

Author.

Studies on calcium carbide. V~VI. V. Melting point diagram of system CaC_2-CaO. N. Kameyama and Y. Inoue. *J. S. C. I. J.* **46**, 1–5 (1943).—Pure CaO and $Ca(CN)_2$ were prepared and the calcd. quantities of CaO, $Ca(CN)_2$ and C (wood charcoal) were mixed and pressed into cakes and were heated in a vacuum elec. furnace. Thereby $Ca(CN)_2$ was changed into CaC_2 and thus the required mixt. of CaC_2 and CaO was prepared. This cake of CaC_2 and CaO was put in a graphite container of cylidrical shape, and a tungsten rod was put on the top of the cake, and the whole was heated in the vacuum elec. furnace. When a certain temp. was reached, the tungsten rod sank suddenly and this point was considered as the temp. at which the whole cake was just molten. This temp. must be equal to the temp. at which the first crystal is formed by cooling from the molten liquid of CaO and CaC_2. The melting point diagram shows several max. and min. The min. is the eutectics, and the max. corresponds to the following compds.:—

	CaC_2-Content	M. pt.
$5CaC_2$–$3CaO$	65.6%	2080°C
or $3CaC_2$–$2CaO$	63.2	
CaC_2–CaO	53.3	2080

$2CaC_2$–$3CaO$	43.3	1930
CaC_2–$2CaO$	36.4	2000

VI. Melting points of commercial carbide of calcium: While the melting points of the system CaC_2-CaO are all above 1850°C, those of commercial carbide are much lower than those of pure CaC_2-CaO system of the corresponding CaC_2-contents, and there are not found any simple relation between the melting points, or the softening points and CaC_2 content, or the sum total of SiO_2, Fe_2O_3, MgO, etc. Authors.

Diffusion of heavy water. S. Kaneko. *Bull. Electrotechn. Lab.*, **7**, 22 (1943).—Theory of diffusion previously reported is applied to the problem of the diffusion of heavy water. Author.

An empirical equation for calculating the changes in the boiling points of hydrocarbons for small changes in pressure. R. Negisi. *Bull. C. S. J.*, **17**, 477—485 (1942).—An empirical relation, $\frac{dt_b°C}{dp_{mm}}=0.0345+0.000111t_b$, in which t_b is the normal boiling point, for calcg. the changes in the boiling points for small changes in the press. has been derived. It has been found that the equation is applicable to most of the hydrocarbons, with their boiling points ranging from −160 to 300°C, with a max. deviation of about ±0.002°C. A comparison of this eq. with the others found in the literature has been made, and it has been found that the relation is just as accurate as some of the more complicated ones proposed. Author.

On the thermal conductivity of binary systems: CO-CO_2 and air-acetone. F. Isikawa and K. Yagi. *Bull. Inst. Phys. Chem. Research*, **22**, 1, 12～17 (1943). The thermal conductivity of the binary systems mentioned above has been measured at 25°. For the unary systems CO and CO_2 the press. (P) and the thermal conductivity (V) (expressed in volts) are related as follows: $P+A=BP/V$ where A and B are the consts. For the binary system the thermal conductivity of the mixt. V may be expressed as a linear function of percentage of CO, that is, the mixt. law may be applied to this system. The value ϵ in the eq. $K=\epsilon\eta C_v$, where K= thermal conductivity, η=viscosity, C_v=specific heat at const. volume, has been found to be 1.7 for CO_2, based on the exptl. result and $\epsilon_{CO}=1.88$. This value is in good agreement with 1.75 obtained from the kinetic theory of gas. The thermal conductivity of the air-acetone system has been measured at total press. 200, 500, 760 mm, the acetone content being up to 11.74%. All the conductivity curves show a small neg. deviation from the mixt. law. From the above results CO in CO_2 can be measured with the accuracy of 0.12% and acetone in the air with the accuracy of 0.05～0.06%. Authors.

The addition of hydrogen bromide to crotononitrile. M. Takebayasi. *J. Chem. Soc. Japan*, **64**, 41–43 (1943).—In the absence of oxygen or air, an oily substance is produced by the addition of hydrogen bromide to crotononitrile. On the hydrolysis of the product by means of mineral acids, β-bromobutyric acid and its amide are obtained. The oily product might be β-bromobutyronitrile (the normal addition product). Then, the polarization of the ethylenic linkage of crotononitrile is suggested to be: $CH_3\cdot\overset{+}{C}H:\overset{-}{C}H\cdot CN$. The negativity of the nitrile-group is considered. The oxygen- (or peroxide-) effect is not recognized in this addition reaction. For this reason, the question is considered whether the normal addition of hydrogen bromide is comparatively more rapid than the abnormal addition, or whether the same product is gielded in the both cases. Author.

The effect of inorganic substances on the carbonization of paper. T. Tatibana. *J. Chem. Soc. Japan*, **63**, 1053–1057 (1942).—The effect of inorganic substances on

the carbonization of paper is studied with filter paper. When inorganic substances are present, the decompn. temp. is lowered and the decompn. velocity falls. The processes of decompn. are classified into 3 groups—(1) the decompn. and simultaneous ignition (2) slow decompn.; (3) the inflammation of carbon in spite of the slow decompn. This is explained by the assumption that the inorganic substances present induce contact-catalytic action in carbonization. J. C. L.

2—SUB-ATOMICS, RADIOCHEMISTRY AND PHOTOCHEMISTRY

On the life-time of neutral vector mesons. S. Nakamura. *Proc. Phys.-Math. Soc. Japan*, 16, 201–209 (1943).—Sakata and Tanikawa proposed a theory of the natural decay of neutral mesons. It was to the following effect: by the interaction of proton a neutral meson is transformed intermediately into a pair of proton and negative proton and then this proton pair is annihilated, emitting more than two photons. Through this process the proper energy of one neutral meson can be transformed into many photons. Therefore neutral mesons may be unstable for this process and have finite life-time in vacuum. If we take vector model for the neutral meson field the probability of decay becomes max. when three photons are emitted; and the life time τ_0 of neutral mesons runs in this case as follows: (I) $\tau_0 \sim 10^{-16}$ sec. There is, however, the approximation in the result (1) that all the products of perturbing terms of the transition and of the numerical coeffs. are taken as 1. To calculate this more precisely is the end of this paper. There appears, however, in the way of the calc. the divergence of the integral to the momentum of proton pair in the inter mediate state. To get rid of this difficulty and obtain the convergent result, the author made the following two attempts: the results of calc. are: (II) the momentum of the virtual proton pair is cut off at 0.3 MC $\tau_0 = 2 \times 10^{-9}$ sec. (III) the diverging integral is excluded ($g_1 = 0$, g_2 retain) $\tau_0 \sim 2 \times 10^{-6}$ sec. ($g_1 = 0$, $g_2 \neq 0$). The expt. by Schein shows that the hard component which penetrates 4～18 cm. thick Pb in the upper atmosphere gives no shower. Taketani suggested that there occurs the theoretical difficulty if we accept Sakata-Tanikawa process and the value of τ_0 as small as (I), assuming the hard component consist of protons. However, this difficulty disappears if neutral mesons are as stable as shown in (II) and (III). It is because they pass through Schein's Pb before they decay into γ-rays.

Author.

On the total cross section of carbon for various resonance neutrons. M. Kimura. *Proc. Imp. Acad. Tokyo*, 18, 367–368 (1942).—The total cross sections of carbon for the "C", "D", "I_1", and "I_2" neutrons were found to be equal within the limit of exptl. errors. It was calcd. with a geometrical correction assuming a symmetrical scattering, and a value of 4.8×10^{-24} cm^2 for all neutron groups was obtained. This is in agreement with the results of Goldhaber and Briggs whose measurements were limited to thermal neutrons. Author.

On the variation in scattering and absorption cross sections by resonance neutron energy. M. Kimura. *Proc. Imp. Acad. Tokyo*, 18, 369–376 (1942). The scattering and absorption cross sections were measured for Fe, Ni, Pb, Zn, Al, Hg, Cl, Co, Mn, Ag and I with various resonance neutrons by the method of back scattering. (I) The scattering cross section of the so-called

good scatterers, such as Ni and Fe, is independent of neutron energy with a tendency toward a slight decrease with higher neutron energy. (II) It shows a max. for the neutron energies corresponding to the resonance absorption levels excluding the 1/v increase in absorption in the region of thermal energies. (III) It has larger values for the neutron energies higher than the resonance levels than for those of lower energies; that is, its value becomes larger when the neutron energy increases beyond a resonance level of the scattering nucleus. (IV) The behaviour in the scattering c.s. of Hg with neutron energy is explained on the assumption of the existence of a resonance level in the neg. energy region not far from zero. Author.

Spectra of γ-rays of 52 V and 56 Mn. Laboratory of Atomic Nucleus, Osaka Imp. Univ. *Proc. Phys.-Math. Soc. Japan*, **III, 24**, 818–820 (1943). — The spectra of γ-rays of 52 V and 56 Mn are studied by means of the magnetic spectro-meter having high analytical activity. The γ-ray of 52 V is simple, its energy being 1.44±0.02 MeV; that of 56 Mn consists of three lines, each having energy of 0.866±0.0008, 1.83±0.02, or 2.11 ±0.02 MeV. The intensity ratio of these lines is 5.5 : 1.5 : 1. J. C. L.

Electric discharge process in the Geiger-Müller counting tube. II-III. O. Minakawa. *Proc. Imp. Acad. Tokyo*, **18**, 644–651 (1941), and **19**, 19–25 (1943).—The electric discharge in the Geiger-Müller counting tube contg. alcohol and argon is observed by means of an oscillograph and the mechs. of "Nachentladung" (N. E.) and "Spontanentladung" (S. E.) studied. N. E. is ascribed to the secondary electron emitted from the wall of cathode by positive ion and S. E. is ascribed to the cold emission by strong elec. field produced by the attachment of positive ions on the cathode. III. From the exptl. results reported in I and II the mech. of elec. discharge of the Geiger-Müller counting tube contg. alcohol and argon, N. E. appears, showing that they are unfit for the counting tube, while He and Ne are usable. The mech. of the tube in which grid glow tube is used is also discussed. J. C. L.

Atomic energies of d^7 and d^6s configurations including configuration interaction. A. Amemiya, T. Isidu and S. Sueoka. *Proc. Phys.-Math. Soc. Japan*, **24**, 7, 584–599 (1942). —The atomic energies of d^7 and d^6s configurations have been calc'd. by the method due to Yamanouti, and the results have been compared with the observed values of FeII $3d^7$ and $3d^64s$. The agreement is satisfactory for d^7 configuration, while there are some discrepancies for d^6s. The configuration interaction between d^7 and d^6s has been also included, but no reasonable value is obtained for the interaction parameter from the exptl. data. Therefore the discrepancies between the calcd. and the observed values can not be explained by the configuration interaction. Authors.

New effects in phosphorescence. T. Takeuti and I. Yosimura. *Bull. Tokyo Univ. Eng.*, **11, 10**, 330–331 (1942). — With zinc sulphide phosphor the resonance phosphorescence and the sensitization of the phosphor by pre-illumination with weak light were found to take place. The blurred scintillation due to radioactive substance is explained as statistical fluctuation. Authors.

Analysis of naphtha by the Raman effect. S. Mizusima and T. Wada. *Bull. Inst. Phys. Chem. Research*, **152**, 1–14 (1942). —Hydrocarbon mixtures are analysed by using the Raman effect and the following problems, which have been hard to solve by the ordinary chem. analysis are solved: (i) detn. of the purity of the standard fuel, *n*-heptane and isooctane, (ii) detn. of the kind of isomer of the isooctane made by polymerizing iobutylene, and (iii) detn. of the composition of the oil formed by the decompn. of oil shale wax. J. C. L.

3—ELECTROCHEMISTRY AND THERMOCHEMISTRY (THERMODYNAMICS)

Equivalent conductivity of 2-2 salts. S. Kaneko. *Bull. Electrotechn. Lab.*, **7**, 31～32 (1943).—Equivalent conductivity of $ZnSO_4$ and $CuSO_4$ is calcd. by the formula already obtained and compared with the observed value. Author.

Calculation of activity coefficient of 2-2 salts by Bjerrum's theory. S. Kaneko. *Bull. Electrotechn. Lab.*, **7**, 37～39 (1943). — Practical method of calcn. of the activity coeff. of 2-2 salts by Bjerrum's theory is considered and applied to the calcn. of the activity coeff. of 2-2 salts. Author.

Studies on the dielectric properties of substances in the sorbed state. II. On the anomalous dispersion of *i*-amyl-alcohol sorbed by titania gel. I. Higuti. *Bull. I. P. C. R.*, **21**, 1138-1146 (1942).—In a range of temp. from 70° to −80°C has been measured the change of capacitance due to the sorbed *i*-amyl alcohol on titania gel which was packed in a cylindrical nickel condenser. In the same way as described in the previous paper, it has been concluded by the analysis of the exptl. results that there are two different types of contribution to the capacitance from the sorptive; one is due to the surface adsorption, that is, to the electronic and atomic polarisation of the sorptive, and the other is due to the capillary condensation of the sorptive, showing a remarkable abnormal dispersion in the temperature range where the ordinary liquid exhibits the same phenomenon. The dielectric const. in the sorbed state has been calcd. and compared with that of the ordinary liquid. Some explanation has been given for the fact that the dielectric const. of the condensed liquid was found to be less than that of the ordinary liquid, by referring to the exptl. result that the dielectric const. increases with the sorbed quantity. Author.

Investigation on the migration of lead atoms in lead accumulators by means of radium D. N. Kameyama and S. Kobayasi. *J. Electrochem. Assoc. Japan*, **11**, 10-17 (1943).—The electrode plates used in the experiments were each $6 \times 7\ cm^2$ and 3 mm thick. Each of them was pasted with PbO and H_2SO_4 mixture. While the paste was still wet a small part was taken and mixed with a few drops of $RaD(NO_3)_2$ soln. and then repasted at the original place. Thus a small area of the electrode plate was inoculated with RaD, and then the accumulator was charged and discharged several times, after which the radioactivity of various parts of the inoculated plate and of the other un-inoculated plate was measured by the Geiger-Müller counter. The counter tube was made of aluminium 0.1 mm thick, through which γ ray of RaD (the isotope of Pb) and β and γ ray of RaE (the isotope of Bi) were passed. The results are discussed from various points of view and the following conclusion is reached. Lead atoms in the plate move mainly by the exchange of atoms. The electrolytic migration of Pb^{++} ion (due to transport number) during charge and discharge is small. The exchange of Pb atoms between the soln. and the particles of the active materials is less when the active material is in the state of PbO_2 (that is Pb^{++++} ions are surrounded by $O^=$) than it is in the state of $PbSO_4$ (that is Pb^{++} ions are surrounded by $SO_4^=$) or in the state of Pb (that is Pb^{++} ions and free electron). Authors.

Thermochemical studies of the acetylation reaction of cellulose in fibrous state. I—III. I. Determination of the gross heat of reaction by the acetylation of cellulose in fibrous state. N.

Saito. *Kogyo-kagaku Kaisi*, **45**, 10, 1122–1130 (1942).—The status of the investigation of the heat of acetylation is briefly given with a short comment. The author started a thermochemical study in comparison with chem. analytical data first on the acetylation of cellulose in the fibrous form. The gross heat that is evolved on the occasion of this acetylation reaction is treated. The huge evolution of heat at the outset of this reaction and the uncertainty of the end point toward the end of the reaction make the cases somewhat complicated. But by obtaining acetylation degree-integral heat curve, the gross heat of reaction up to 100% acetylation is detd. by extrapolation. The gross heat thus obtained is somewhat different according to the starting cellulose materials, ramie, cotton, or α-pulp and also to the sorts of acetylating baths I or II employed; and it ranged between 80 and 100 k cal/$C_6H_{10}O_5$. **II. The separation of the initial heat of acetylation, and the total heat of the acetylation reaction, up to 100% esterification.** The gross heat obtained in (I) is the sum of the heat of reaction in the initial stages as well as the reaction in the acetylation process itself. The two sorts of heats are treated separately and the latter part is calcd. out, which amounts to 53–54 k cal/$C_6H_{10}O_5$, independent of the sorts of cellulose materials and the kinds of acetylating baths I and II. **III. The thermal analysis of the acetylation reaction of cellulose in fibrous state.** In the previous reports a peculiality of the acetylation reaction of cellulose was mentioned and the gross heat of the reaction obtained by the method of analysis stated therein up to 100% esterification (Q_g); and also the total heats that pertained in the acetylation process itself (Q_x) were calcd. Here the kinetics of the heat evolution is studied, and the notable result is elucidated that, after rapidly passing the initial and the earlier stages, the process of the heat evolution in the acetylation reaction region follows the 1st order reaction velocity equation in all cases with ramie, cotton and α-pulp.

Author.

4—COLLOID CHEMISTRY AND SURFACE CHEMISTRY
(CONTACT CATALYSIS)

Studies on the iron catalyst used for the synthesis of petroleum by X-rays. I. S. Kodama and H. Tahara. *J. Soc. Chem. Ind. Japan*, **45**, 1260–1263 (1942).—For the purpose of investigating the nature of an iron catalyst and the decline in its activity, the change of the crystal state during the course of the synthesis reaction is studied by X-ray analysis. The original iron catalyst (Fe+25%Cu+2%Mn+125% diatom earth+2%K_2CO_3) has not any definite form when examined by X-rays. When it is treated at 700°, it turns into α-Fe_2O_3. When it is reduced with hydrogen at 450°, it loses its activity. Further, when it is oxidized at 250°, it becomes a crystal of spinel type, though not restoring its activity. J. C. L.